

THE GAS-CHROMATOGRAPHIC ANALYSIS OF COKE-OVEN
BENZENE-TOLUENE-XYLENE (BTX),
BENZENE-TOLUENE (BT), AND BENZENE
FOR MINOR COMPONENTS

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Introduction

Rapid methods for analyzing coke-oven benzene-toluene-xylene (BTX), benzene-toluene (BT) and benzene fractions for minor components are necessary to supplement purification processes for improving the quality of the benzene, toluene, and xylene fractions of light oil. During the investigation of methods for removing sulfur-containing compounds and other impurities from BTX and BT fractions, it was suspected that catalyst poisoning and the formation of undesirable resins were caused at least in part by cyclopentadiene, which occurs in such fractions when they are first collected. Since cyclopentadiene dimerizes easily, a method of analyzing for both the monomer and the dimer was desired. Along with the investigation of purification processes, one of the recurring analytical problems in our laboratory is the determination of trace impurities in refined light-oil products. The cyclohexene, cyclohexane, and methylcyclohexane contents of benzene were of particular interest.

Colorimetric methods for detecting and determining cyclopentadiene (1,10,13) and dicyclopentadiene (6,13) have been reported. Methods in which a maleic anhydride reaction (3,9) is utilized have been published. The condensation reaction between cyclopentadiene and aldehydes or ketones to form highly colored fulvenes has been used for the quantitative determination of cyclopentadiene and dicyclopentadiene in hydrocarbon mixtures (7). Techniques that involve saponification (2) and bromination (5,12) have been investigated. Infrared (11) and ultraviolet (8,14) spectrophotometric techniques have been published for determining cyclopentadiene and dicyclopentadiene in hydrocarbon mixtures. Various procedures, including mass spectrometry and infrared spectroscopy, can be used to determine the paraffin content of aromatic hydrocarbons. The total paraffin content of benzene is obtained by the ASTM sulfonation procedure D851-47.

Most of these methods are complicated by difficulties associated with interfering compounds, lengthy analysis times and, in some instances, poor sensitivity. The ASTM method for paraffins is not applicable to the analysis of specific paraffins. Mass-spectrometric and infrared spectrophotometric methods are much too difficult, if not impossible, for use in the hydrocarbon concentration ranges of particular interest in this investigation.

The purpose of this paper is to describe the apparatus and materials used in developing gas-liquid chromatographic methods of analysis for determining (1) cyclopentadiene and dicyclopentadiene in BTX and BT fractions, and (2) cyclohexene, cyclohexane, and methylcyclohexane in benzene.

Experimental

Apparatus

The instrument used was the Perkin-Elmer Corporation Model 154-B Vapor Fractometer. A 0-10 millivolt recorder (Leeds-Northrup Co.) was used for the cyclopentadiene and dicyclopentadiene methods. For the cyclohexene, cyclohexane, and methylcyclohexane method, the same instrument was converted to a 0-1 millivolt recorder. Samples were introduced into the instrument through the liquid sample-handling valve by means of uncalibrated Perkin-Elmer capillary pipettes. Helium was used as the carrier gas. The columns and standard operating conditions for each method are listed in Table I.

Materials

The following reagents were used as standards. Phillips Petroleum Company Research Grade benzene was used in developing the methods for the analysis of cyclopentadiene and dicyclopentadiene in BTX and BT. A commercial benzene, containing a negligible amount of cyclohexane and methylcyclohexane as the only non-aromatic impurities, was used in developing the method for trace amounts of cyclohexene, cyclohexane, and methylcyclohexane in benzene. The dicyclopentadiene (95.6 wt % pure) was obtained from the Matheson Company. The cyclopentadiene was prepared by depolymerizing a portion of Matheson dicyclopentadiene, fractionating the depolymerized product, and recovering the cyclopentadiene fraction. The cyclopentadiene obtained by this method was 89.2 mole per cent pure, as determined by gas-liquid chromatography and mass spectrometry. The cyclohexene, cyclohexane, and methylcyclohexane were Phillips Petroleum Company Research Grade.

Procedure

Synthetic mixtures containing 0-2 weight per cent cyclopentadiene in benzene, 0-0.7 weight per cent dicyclopentadiene in benzene, and 0-0.5 weight per cent each of cyclohexene, cyclohexane, and methylcyclohexane in benzene were prepared. In the latter mixtures, the concentrations of the three components were varied independently, and dilutions of these mixtures were made, to provide solutions in which the concentrations of each component covered the three concentration ranges, 50-500, 5-50, and 0-5 parts per million (ppm).

All mixtures were chromatographed under the standard operating conditions. The gas-chromatographic data were corrected for purity of the standards, and calibration curves were prepared in which peak heights were related to concentration. The calibration curves were linear for all compounds in all concentration ranges investigated. In measuring the height of a peak, both in synthetic mixtures and in samples analyzed, the net height above the base line was always used.

With the peak-height and concentration data obtained in the investigation of the synthetic mixtures of cyclohexene, cyclohexane, and methylcyclohexane in benzene, equations were derived by the method of least squares; these equations were used to calculate the concentrations of cyclohexene, cyclohexane, and methylcyclohexane in benzene.

Results and Discussion

In the preliminary experimental work associated with the analysis of BTX and BT for cyclopentadiene, a 20-microliter sample of crude BTX was chromatographed under standard operating conditions. The resulting chromatogram, Figure 1,

in the range of interest (emergence time, 0 to 12 min), revealed one major peak and five minor peaks. When 20 microliters of a solution of approximately 0.5 weight per cent cyclopentadiene in benzene was chromatographed under identical conditions, the retention time for cyclopentadiene was very nearly equal to the retention time of peak number 1, Figure 1. The substance producing this peak in the chromatogram of the sample was tentatively identified as cyclopentadiene.

To confirm this tentative identification, the substance producing peak number 1, Figure 1, was trapped from the vent line of the gas chromatograph in a trap cooled in liquid nitrogen, and the material collected was analyzed by mass spectrometry. It was almost entirely cyclopentadiene. A very small concentration of an unidentified constituent was also detected. This impurity may have had a retention time similar to that of cyclopentadiene, but its concentration was so low that it could cause only negligible errors.

Not shown in Figure 1 is the remaining portion of the chromatogram (emergence time, 12 to 174 min), which revealed 11 additional peaks attributed to thiophene, toluene, the xylene isomers, dicyclopentadiene, and other unidentified constituents. These compounds were of no interest in the development of this method, except that they had to be removed from the column before another sample could be analyzed. Therefore, they were removed by back-flushing the column, a technique that reduces the time of analysis from 175 minutes (at standard operating conditions) to approximately 15 minutes. Only slight modifications of the flow system of the instrument and a few additional manipulations of controls are required.

Mass-spectrometric analysis of the cyclopentadiene used as a standard in this investigation indicated the presence of 10.1 mole per cent dicyclopentadiene. Because a pure cyclopentadiene standard was not available for comparison, it was not practicable to determine accurately the purity of the cyclopentadiene used. However, a reasonable estimate of the purity was deduced from the fact that the gas-liquid chromatogram of a 20-microliter sample of the cyclopentadiene standard revealed one major peak and eight minor peaks. None of the peaks represented the dicyclopentadiene in the sample because the retention time of this compound is much greater at the standard operating conditions than any constituent shown. No attempt was made to identify the minor peaks present in the chromatogram. However, if the thermal conductivities of the substances representing the minor peaks are assumed to be equal to that of cyclopentadiene, the combined unidentified impurities total 0.7 per cent. Consequently, the cyclopentadiene used as the standard for developing this method was assumed to be 89.2 mole per cent pure.

The average absolute error obtained in the analysis of a series of synthetic mixtures that contained 0 to 2 weight per cent cyclopentadiene was ± 0.01 weight per cent. The least detectable concentration of cyclopentadiene by the procedure described is 0.05 weight per cent.

In the preliminary experimental work associated with the analysis of BTX and BT for dicyclopentadiene, a 200-microliter portion of a silica-gel-treated BT was chromatographed under the standard operating conditions. The resulting chromatogram, Figure 2, revealed four major peaks and several minor peaks. Peak numbers 1, 2, 3, and 4 represent the benzene, toluene, xylenes, and unknown fractions of the sample. When a 200-microliter sample of a 1.4 weight per cent solution of dicyclopentadiene in benzene was chromatographed under the same conditions, the retention time for the dicyclopentadiene was very nearly equal to the retention

time of peak number 4, Figure 2. It appeared that this peak in the chromatogram of the sample was due, at least in part, to dicyclopentadiene.

This tentative identification was confirmed by the previously described gas-chromatographic mass-spectrometric analysis. The substance causing this peak in the chromatogram of the sample was mainly dicyclopentadiene with a very small proportion of a C₉ aromatic. The concentration of the C₉ aromatic was so small that any error it might cause would be negligible.

It was necessary to introduce a large quantity (200 microliters) of the sample into the instrument to obtain a measurable height for peak number 4. Although this peak appears to be relatively large in Figure 2, it was barely perceptible in the chromatogram of 200-microliter portions of several other BT samples examined.

The chromatogram of a 10-microliter sample of the Matheson dicyclopentadiene used as the standard in this determination displayed one major impurity peak. If the thermal conductivity of the substance causing this peak is assumed to be equal to that of the dicyclopentadiene, the Matheson dicyclopentadiene is 95.6 weight per cent pure. This value is based on the assumption that the major peak in the chromatogram is caused only by dicyclopentadiene. To confirm this assumption, this peak was trapped and analyzed by mass spectrometry. In addition to dicyclopentadiene, only traces of a C₉ aromatic were identified.

The method developed for determining dicyclopentadiene in BT was used to determine dicyclopentadiene in 18 samples in duplicate of crude BT or materials derived from it. The results of these analyses indicated that the average repeatability of the method is approximately 0.001 weight per cent over the range from 0 to 0.3 weight per cent dicyclopentadiene. The least detectable concentration of dicyclopentadiene by this method is 0.01 weight per cent. The time required for one measurement is approximately 10 minutes.

In the preliminary experimental work associated with the analysis of benzene for cyclohexene, cyclohexane, and methylcyclohexane, a 50-microliter portion of a sample of 1°-benzene was chromatographed under the standard operating conditions. The resulting chromatogram, Figure 3, revealed several peaks preceding the benzene peak. Tentative identification of the peaks was accomplished by chromatographing a portion of a synthetic blend of hydrocarbons in benzene and comparing the retention-time data of the synthetic blend with the retention-time data of the sample. Figure 4 illustrates the resolution of several hydrocarbons (Table II) obtained under the standard operating conditions.

To confirm the tentative identifications, the impurities of the sample of 1°-benzene were concentrated by progressive freezing, as described by Glick (4). This procedure was necessary because the impurities were in the ppm range. The concentrated impurities were chromatographed under the standard operating conditions, and the substances producing the unknown peaks were trapped as previously described and analyzed by mass spectrometry. By use of this technique, the major impurities were found to be n-heptane, cyclohexane, and methylcyclohexane (peaks no. 1, 2, and 3, respectively, of Figure 3). No cyclohexene was detected. The minor peaks shown in the chromatogram were attributed to small amounts of other hydrocarbon impurities.

Some difficulty was experienced in obtaining a paraffin-free benzene to be used as a standard in the preparation of synthetic mixtures. A commercial benzene was found that was almost completely paraffin-free. When a 500-microliter

portion of this benzene was chromatographed under operating conditions selected to give maximum sensitivity, the chromatogram, Figure 5, revealed two small peaks (peaks no. 1 and 2) preceding the benzene peak. These peaks were attributed to cyclohexane and methylcyclohexane, respectively, and their concentration was found to be approximately 2 ppm each.

The method developed for the determination of trace impurities in benzene was used to analyze several samples of benzene for cyclohexene, cyclohexane, and methylcyclohexane. The results of these analyses indicated that the average repeatability of the method is approximately 1 ppm over the range of 0 to 50 ppm and approximately 3 ppm over the range of 50 to 500 ppm for both cyclohexane and methylcyclohexane. No cyclohexene was detected in any samples analyzed. The lower limit of detection for each of the compounds was approximately 1 ppm. This value could probably be lowered by utilizing an amplifier to increase the signal from the detector. For the concentration ranges of 50-500, 5-50, and 0-5 ppm, the standard deviations for the respective compounds in the analysis of synthetic mixtures are shown in Table III.

Acknowledgements

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Literature Cited

- (1) Afanas'ev, B. N., Ind. Eng. Chem., Anal. Ed., 8, 15 (1936)
- (2) Bergmann, F., Japhe, H., Anal. Chem., 20, 146 (1948)
- (3) Birch, S. F., Scott, W. D., Ind. Eng. Chem., 24, 14 (1932)
- (4) Glick, C. F., Miskalis, A. J., Kessler, T. K., 136th National Meeting of the American Chemical Society, Atlantic City, New Jersey
- (5) Hammick, D. C., Langrish, D., J. Chem. Soc., 797 (1937)
- (6) Palfray, L., Sabetay, S., Kadrinoff, B., Ann. Chim. Anal. Chim. Appl., 23, 207 (1941); Chem. Zentr., 1942, 11, 2724
- (7) Powell, J. S., Edson, K. C., Fisher, E. L., Anal. Chem., 20, 213 (1948)
- (8) Powell, J. S., Edson, K. C., Ibid, 20, (1948)
- (9) Sefton, R., J. Soc. Chem. Ind., 64, 104 (1945)
- (10) Shuikin, N. I., Tulupov, V. A., Zhur. Obshchei Khim., 24, 2199 (1954)
- (11) Takeuchi, T., Tanaka, S., Coal Tar (Japan), 7, 356 (1955)
- (12) Tomicek, O., Blazek, A., Roubal, Z., Chem. Zvesti, 4, 479 (1950)
- (13) Uhrig, K., Lynch, E., Becker, H. C., Ind. Eng. Chem., Anal. Ed., 18, 550 (1946)
- (14) Vraný, M., Bohdanecký, M., Chem. Listy, 49, 936 (1955)

Table I

STANDARD OPERATING CONDITIONS

<u>Condition</u>	<u>Determination</u>		
	<u>Cyclopentadiene in BTX and BT</u>	<u>Dicyclopentadiene in BTX and BT</u>	<u>Cyclohexene, Cyclo- hexane, and Methyl- cyclohexane in Benzene</u>
Column	6 ft x 0.375 in. of o- and p- Benzylbiphenyls, 24% on Fisher Column Packing	12 ft x 0.25 in. of Dow Corning Silicone Stopcock Grease, 25% on Burrell Inert Carrier	20 ft x 0.25 in. of Paraplex U-148, 25% on Burrell Kromat-FB, and 14 ft x 0.25 in. of Paraplex G-54, 20% on Burrell Kromat-FB
Temperature (°C)	60	140	100
Pressure (psig)	5	25	20
Flow (ml/min)	210	330	50
Detector Voltage (volts)	8	8	8
Sample Size (μ l)	20 (nominal)	200 (nominal)	50 (nominal) 500 (nominal)
Recorder Range (mv)	0-10	0-10	0-1

Table II

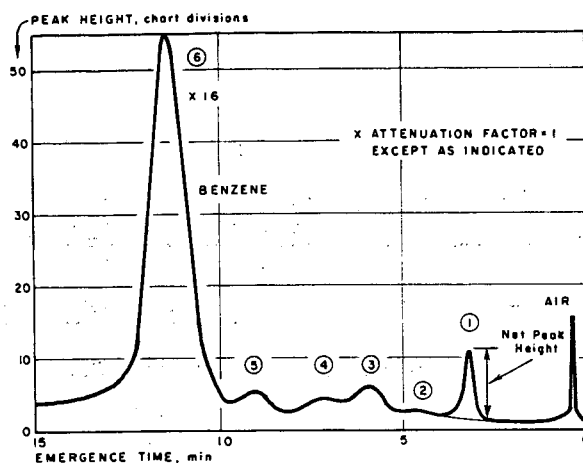
ABBREVIATED NOMENCLATURE OF C₅ TO C₈ HYDROCARBONS USED IN THE SYNTHETIC
BENZENE-PARAFFIN MIXTURE

<u>Compound</u>	<u>Abbreviated Nomenclature</u>
n-Pentane	n-P
2-Methylpentane	2-MP
n-Hexane	n-Hex
2,4-Dimethylpentane	2,4-DMP
Cyclopentane	CP
2-Methylhexane	2-MHex
3,3-Dimethylpentane	3,3-DMP
3-Methylhexane	3-MHex
Methylcyclopentane	MCP
2,3-Dimethylpentane	2,3-DMP
2,2,4-Trimethylpentane	2,2,4-TMP
3-Ethylpentane	3-EP
n-Heptane	n-Hep
1,1-Dimethylcyclopentane	1,1-DMCP
Cyclohexane	CHexane
2-Methylheptane	2-MHep
3-Methylheptane	3-MHep
Methylcyclohexane	MCH
n-Octane	n-Oct
Cyclohexene	CHexene

Table III

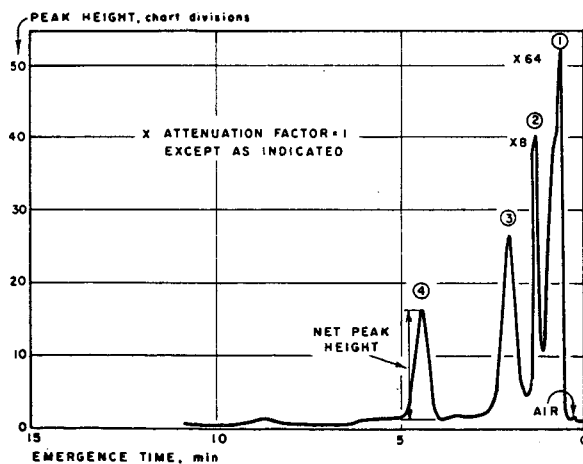
STANDARD DEVIATIONS OBTAINED IN THE ANALYSIS OF SYNTHETIC MIXTURES OF
CYCLOHEXENE, CYCLOHEXANE, AND METHYLCYCLOHEXANE IN BENZENE

<u>Concentration Range, ppm</u>	<u>Standard Deviations, ppm</u>		
	<u>Cyclohexene</u>	<u>Cyclohexane</u>	<u>Methylcyclohexane</u>
50-500	4.6	7.7	5.5
5-50	0.7	0.4	0.5
0-5	0.1	0.2	0.3



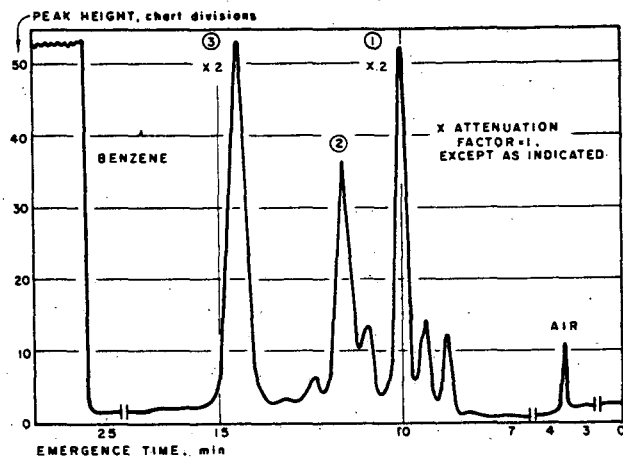
CHROMATOGRAM OF CRUDE BTX

FIGURE 1



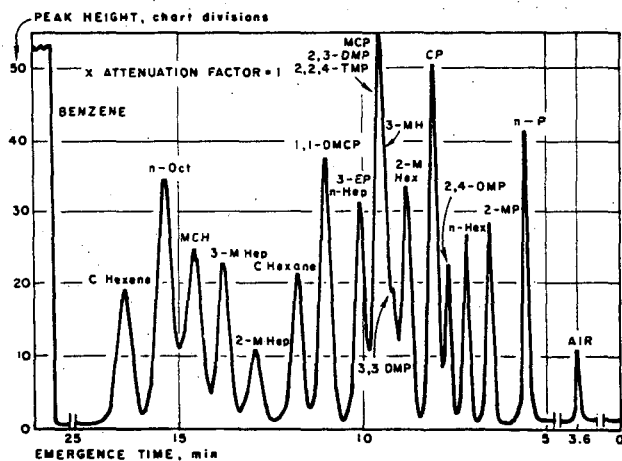
CHROMATOGRAM OF SILICA-GEL-TREATED BT

FIGURE 2



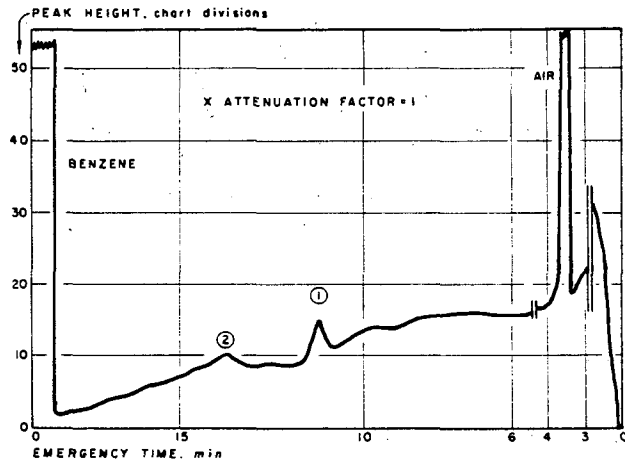
CHROMATOGRAM OF A 1° COKE-OVEN BENZENE

FIGURE 3



CHROMATOGRAM OF A SYNTHETIC MIXTURE OF HYDROCARBONS

FIGURE 4



CHROMATOGRAM OF 1° COKE-OVEN BENZENE USED AS A STANDARD
FIGURE 5